Mass Spectrometry for Chemists and Biochemists, Second Edition

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The first edition of this book was published in 1982, and during the 14-year period between the first and second editions, enormous changes have occurred in mass spectrometry. For example, the most popular mass analyzers for biological mass spectrometry, e.g., time-of-flight (TOF), quadrupole ion traps (QIT), and Fourier transform ion cyclotron resonance (FTICR) instruments, were not even considered viable analytical instruments in 1982. The popular ionization methods of today, electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI), had not even been introduced in 1982. In spite of the revolutionary changes that have occurred in mass spectrometry since 1982, the foundations of the science, viz. the theory and chemistry of mass spectrometry (unimolecular dissociation, ion-molecule reaction chemistry, gas-phase acidity, Bronsted and Lewis acidity/basicity, etc.) and even the objectives of the mass spectrometry experiment have not changed. That is, whether the objective of the mass spectrometry experiment is to obtain the mass spectrum of a volatile organic compound or a complex protein for the purposes of molecular weight determination or structure elucidation or amino acid sequence of a peptide, issues related to the ionization process (absolute ion yields, the types of ions formed, e.g., radical cation of the intact molecule, a protonated molecule, $[M+H]+$, or transition metal cationized form of the molecule), the internal energies of the ions produced, or the fragmentation reactions of the intact ion are all governed by processes that have been carefully studied for several decades. The scope of this book focuses on much of the early work that has dealt with many of the important fundamental issues related to mass spectrometry. Consequently, the material covered in this text is essential for developing a complete understanding of mass spectrometry. The new group of mass spectrometrists that has entered the field since the rapid growth initiated by the introduction of ESI and MALDI, the ionization methods that are largely responsible for the new directions in instrumentation, could benefit by careful study of the fundamentals provided by this book. Although the coverage of the latest innovations in the field that strongly impact biological research, especially molecular biology and materials science, is sparse, the chapters that cover basic mass spectrometry are well written and thorough.

The book is organized into 12 chapters. Chapter 1 covers general features of the mass spectrum. The chapter includes discussion of multiple-charged ions, metastable ions, isotope distributions, and elemental composition. This chapter also contains a section on elemental composition, which leads into a short discussion of mass resolution; however, this section does not adequately address issues of mass resolution, mass measurement accuracy, and elemental composition determinations. Chapter 2 covers instrument design, e.g., sample introduction, ion sources, analyzers, and detectors. The chapter includes sections on the recent innovations in the field, e.g., TOF, QIT, and FTICR instruments, as well as discussion of conventional magnetic sector instruments and Mattauch-Herzog geometry instruments. The reviewer was surprised to find that this chapter also included a discussion of photographic plate detectors and densitometers, neither of which qualify as modern mass spectrometry hardware. The photographic plate detectors have been replaced by spatial array detectors, and this special class of detector is not mentioned in the book. Although there are some deficiencies in the chapter content, it is important to stress that the basic material in this chapter is important to the understanding of how a mass spectrometer works. Thus, for the student of the discipline, this chapter should be viewed as essential material. Chapter 3 is entitled Methods of Ionization and all the major methods of ion production, including ESI and MALDI, are covered. The remaining chapters cover Computers in Mass Spectrometry: Data Systems (Chapter 4), Combined Chromatography and Mass Spectrometry (Chapter 5), Uses of Derivatization (Chapter 6), Quantitative Mass Spectrometry (Chapter 7), Metastable Ions and Mass Spectrometry/Mass Spectrometry (Chapter 8), Theory of Mass Spectrometry (Chapter 9), Structure Elucidation (Chapter 10), Examples of Structure Elucidation by Mass Spectrometry (Chapter 11), and Further Discussion of Selected Topics (Chapter 12).

The chapters that deal with quantitative mass spectrometry (Chapter 7) and metastable ions and tandem mass spectrometry (Chapter 8) are useful chapters for students of the subject and new students in the field. Although much of the material covered in these chapters has been around for some time, the topics are presented well and understanding of this material is essential to many new areas of mass spectrometry. Likewise, Chapter 9 deals with the theory of mass spectrometry and the discussion is based primarily on ions formed by EI; however, understanding the relationship between internal energy and lifetime of the dissociating ion is also important for other ionization

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methods. The basic arguments relating internal energy of the dissociating ion and rates of dissociation hold independent of the method used to produce the ions. In this regard, the section on collision-induced dissociation is well written and with only minor modifications to include some of the recent work on collisional activation theory is sufficient to convey the essential components.

Chapter 10 focuses on interpreting the mass spectral data in terms of molecular structure. Careful reading of this chapter in conjunction with examination of Chapter 11 (Examples of Structure Elucidation by Mass Spectrometry) is useful as a learning exercise. After studying these sections, the student of mass spectrometry will have begun the long journey of developing the necessary tools for using mass spectrometry as a structural characterization method.

The final chapter, Further Discussion of Selected Topics, covers ancillary mass spectrometry experiments. The topics are interesting reading for the more advanced student of the discipline; however, in the reviewers opinion this chapter would have greater impact if the topics were focused on examples of more recent innovation.